

# Concentration-Dependent Diffusion Instability in Reactive Miscible Fluids

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We report new chemoconvective pattern formation phenomena observed in a two-layer system of miscible fluids filling a vertical Hele-Shaw cell. We show both experimentally and theoretically that the concentration-dependent diffusion coupled with the frontal acid-base neutralization can give rise to formation of the local unstable zone low in density resulting in a perfectly regular cell-type convective pattern. The described effect gives an example of yet another powerful mechanism which allows the reaction-diffusion processes to govern the flow of reacting fluids under gravity condition.

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In last decades the interaction between reaction-diffusion phenomena and pure hydrodynamic instabilities has attracted increasing interests both from the fundamental point of view of nonlinear science and from the chemical engineering [1–3]. The interest arises from the fact that the chemically-induced changes of fluid properties such as density, viscosity, thermal conductivity or surface tension may result in the instabilities, which exhibit a large variety of convective patterns.

Scenario for instability development essentially differs for immiscible and miscible systems of liquids. The simple, irreversible chemical scheme such as a neutralization reaction  $A+B \rightarrow S$  occurring in binary liquid-liquid immiscible systems was studied in [4–9]. The pattern formation in the form of irregular plumes and fingers was shown to originate from the coupling between different gravity-dependent hydrodynamic instabilities occurring when an organic solvent containing an acid A is in contact with an aqueous solution of an inorganic base B [4]. This irregularity looked natural since the configuration of more dense acid on top of less dense base in the presence of gravity is unstable via the Rayleigh-Taylor (RT) mechanism [5, 6]. A much more impressive, regular pattern of cellular-like fingers keeping contact with the interface was reported for an organic base [7]. The regularity was shown to originate from the perfect balance between the RT instability on the one hand, and the Rayleigh-Bénard [8] and Marangoni [9] mechanisms on the other. Thus, a liquid-liquid interface was recognized to be important for performing fine-tuning of salt fingers.

A completely different situation was observed in the miscible case. The main engine breaking the equilibrium here was found to be the difference between the diffusion rates of all three substances resulting in double diffusive (DD) instability or diffusive-layer convection (DLC) as well as RT instability [10]. All the works devoted to this subject at a given moment, usually noted the formation of irregular patterns of fingers. For example, recently Almarcha *et al.* [11–13] have shown that the various possible convective regimes can be triggered by acid-base reactions when a less dense acid solution lies on top of a denser alkaline one in the gravity field. The possible dy-

namics are a composition of only two asymptotic cases: irregular plumes induced by a local RT instability above the reaction zone and irregular fingering in the lower solution induced by differential diffusive effects.

Absolutely in all works in this field, cited or not, the diffusion coefficients of species have been assumed to be constant. Generally, a concentration-dependence exists in most systems, but often, e.g. in dilute solutions, the dependence is weak and the diffusion coefficient can be assumed constant [14]. This is especially true for fluid mechanics [15]. Some rare examples of the influence of concentration-dependent diffusion include the colloid ultrafiltration [16] and membrane transport [17] where the basic fluid flow is just slightly modified. Reaction-diffusion problems include the plasma wave dynamics [18] and the Turing instability under centrifugal forces [19].

In this Letter, we also focus on the study of chemo-hydrodynamic processes which accompany a frontal neutralization reaction taking place between two miscible liquids. We report a new type of instability, the *concentration-dependent diffusion* (hereinafter CDD) instability from the family of the double-diffusion phenomena [20]. It arises when the diffusion coefficients of species depend on their concentrations. We demonstrate both experimentally and theoretically that chemically-induced changes of reagent concentrations coupled with concentration-dependent diffusion can produce spatially localized zone with unstable density stratification that under gravity gives rise to the development of perfectly periodic convective structure even in a miscible system.

*Experimental results.* The experiments were performed in a vertically oriented Hele-Shaw cell made of two glass plates (width 2.5 cm  $\times$  height 9.0 cm) separated by a thin gap of 0.12 cm. The cell was filled with aqueous solutions of reagents whose concentration always provided a steady stratified density distribution. We examined a few acid-base pairs formed by HCl or HNO<sub>3</sub> from one side and NaOH or KOH from another. During the filling of the cell with the upper solution, the lower layer was separated by a thin plastic slide inserted in two narrow (0.3 mm) slots made in the walls. Fizeau interferometry was used to visualize a refractive index distribution. The latter was

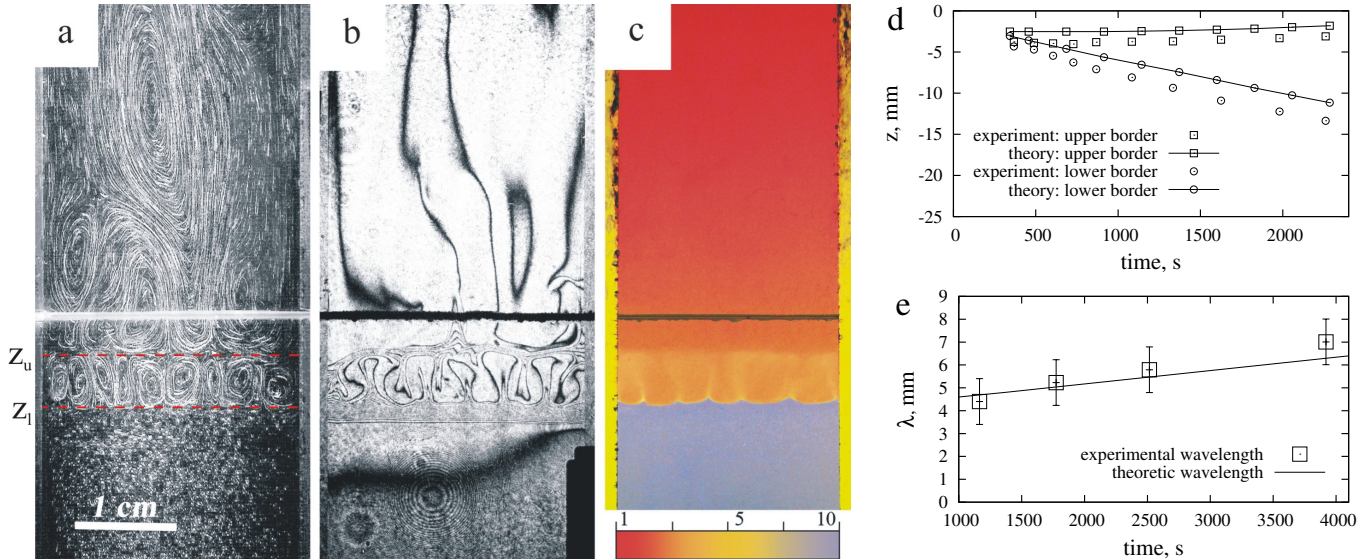


FIG. 1: (a-c) Chemo-convective structures arising due to the CDD instability observed 1100 s after as the aqueous solutions of  $\text{HNO}_3$  (top) and  $\text{NaOH}$  (bottom) were brought into contact in a vertical Hele-Shaw cell: (a) Velocity field revealed by the tracks of light-scattering particles; (b) Interferogram showing a refractive index distribution; (c)  $\text{pH}$  distribution obtained in the presence of color indicator. Initial concentrations of species are both equal to 1 mol/l. The initial contact line is indicated by the horizontal band. (d,e) Evolution of the upper (indicated in (a) as  $Z_u$ ) and lower ( $Z_l$ ) boundaries (d) and wavelength (e) of the CDD pattern in time obtained experimentally (points) and numerically within the theoretical model (lines).

caused by inhomogeneities induced by the concentration distribution of species and reaction exothermicity. The maximum temperature increase measured in the vicinity of the reaction front was found to be near 1 K. In this case the refractive index deviation due to temperature was at least one order of magnitude smaller than that caused by concentration. Thus, the interferograms obtained in the experiments reflected mainly the concentration distribution. Silver-coated hollow glass spheres were added to the liquids to observe the convective patterns which form during the reaction. We visualized also the  $\text{pH}$  distribution by adding a small amount of universal acid-base indicator to the solutions. The comparison of the results obtained with and without the indicator has shown that the presence of the indicator did not influence the instability scenario and pattern formation process, as it was demonstrated in some recent studies [21, 22].

Right after the prepared solutions were brought into contact, the transition zone started to form between them where the reagents were transported towards the reaction front only via the diffusion mechanism. Then the occurrence of a depleted layer just above the diffusion zone has given rise to the formation of plumes which result in the development of weak buoyancy-driven convection in the whole upper layer. A few minutes after the beginning of the experiment, the fluid flow in the form of the periodic array of convective cells (Fig. 1a) has been formed within the diffusion zone just above the reaction front. The cells were arranged between two areas of im-

mobile fluid which definitely indicated the formation of a local “pocket” with the unstable density stratification (Fig. 1b). One can note that the cellular structure did not interact with the convection in the upper layer. The observations of  $\text{pH}$  distribution (Fig. 1c) have shown that above and below the cells band the medium has almost homogeneous  $\text{pH}$  (acidic or alkaline). The  $\text{pH}$  within the cellular pattern is more neutral indicating the accumulation of the reaction product in this zone. Clearly defined zone of the intermediate acidity suggests that we deal here with some kind of a cooperative phenomenon.

We found that the structure can exist for several hours with the band slowly widening with time (Fig. 1d) that results in the wavelength growth (Fig. 1e). It is important to note that this chemo-convective regime was found also in all pairs of reactants used in experiments, but only at certain ratio of initial concentrations (Table 1).

*Theoretical model.* To describe the observed phenomenon of the CDD instability consider two miscible fluids filling a close parallelepiped sufficiently squeezed along one horizontal direction to use a Hele-Shaw approximation [6]. The upper and lower layer are aqueous

TABLE I: Initial concentrations ratio  $\mu$  of different acid-base pairs for which the cellular chemostructure has been observed.

Acid:Base	$\text{HNO}_3:\text{NaOH}$	$\text{HNO}_3:\text{KOH}$	$\text{HCl}:\text{NaOH}$
$\mu$	1 : 1	1 : 1.3	1 : 0.7

solutions of acid  $A$  and base  $B$  respectively. Right after the process starts, the acid and base diffuse into each other and are neutralized with the formation of salt  $S$  with the rate  $K$ . The system geometry is given by two-dimensional domain with  $x$ -axis directed horizontally and  $z$ -axis anti-directed to gravity. We choose the following characteristic scales: length - the gap-width  $h$ , time -  $h^2/D_{a0}$ , velocity -  $D_{a0}/h$ , pressure -  $\rho_0\nu D_{a0}/h^2$  and concentration -  $A_0$ . Here  $D_{a0}$ ,  $\rho_0$ ,  $\nu$ ,  $A_0$  define constant acid diffusivity, solvent density, kinematic viscosity and initial acid concentration respectively. The mathematical model we develop consists in the set of reaction-diffusion-convection equations coupled to Navier-Stokes equation, written in the dimensionless form:

$$\Phi = -\nabla^2\Psi, \quad (1)$$

$$\frac{1}{Sc} \left( \partial_t \Phi + \frac{6}{5} J(\Psi, \Phi) \right) = \nabla^2 \Phi - 12\Phi - R_a \partial_x A -$$

$$-R_b \partial_x B - R_s \partial_x S, \quad (2)$$

$$\partial_t A + J(\Psi, A) = \nabla D_a(A) \nabla A - \alpha AB, \quad (3)$$

$$\partial_t B + J(\Psi, B) = \nabla D_b(B) \nabla B - \alpha AB, \quad (4)$$

$$\partial_t S + J(\Psi, S) = \nabla D_s(S) \nabla S + \alpha AB, \quad (5)$$

where  $J$  stands for the Jacobian determinant  $J(F, P) \equiv \partial_z F \partial_x P - \partial_x F \partial_z P$ . Here we use a two-field formulation for motion equation, and introduce the stream function  $\Psi$  and vorticity  $\Phi$  defined by (1). Eq. (2) differs from a standard Navier-Stokes equation by the additional term  $12\Phi$  which is responsible for the average friction force due to the presence of the side-walls. Diffusion terms in Eq. (3-5) have been written in the most general form [14].

The problem parameters are the Schmidt number  $Sc = \nu/D_{a0}$ , the Damköhler number  $\alpha = KA_0h^2/D_{a0}$  and the set of solutal Rayleigh numbers for species  $R_i = g\beta_i A_0 h^3 / \nu D_{a0}$ ,  $i = \{a, b, s\}$ . Their values for the pair  $\text{HNO}_3 / \text{NaOH}$  (see Table 1) have been estimated as follows:  $Sc = 10^3$ ,  $\alpha = 10^3$ ,  $R_a = 1.5 \times 10^3$ ,  $R_b = 1.8 \times 10^3$ ,  $R_s = 2.4 \times 10^3$  (see Supplementary information B).

The boundary conditions for Eqs. (1-5) are

$$\Psi = 0, \quad \partial_i \Psi = 0, \quad \partial_i A = 0, \quad \partial_i B = 0, \quad \partial_i S = 0, \quad (6)$$

where  $i = \{x, z\}$  for side-walls and horizontal boundaries respectively. The initial conditions at  $t = 0$  are

$$\begin{aligned} z \leq 0: \quad & \Psi = 0, \quad \partial_z \Psi = 0, \quad A = 0, \quad B = 1; \\ z > 0: \quad & \Psi = 0, \quad \partial_z \Psi = 0, \quad A = 1, \quad B = 0. \end{aligned} \quad (7)$$

We found that a concentration-dependence of diffusion plays an important role in the pattern formation. Thus, in Eq. (3-5) the diffusion coefficients have been assumed to be not constant, but depend on their own concentration:  $D_a(A)$ ,  $D_b(B)$  and  $D_s(S)$ . In order to evaluate the diffusion formulas for the pair  $\text{HNO}_3/\text{NaOH}$ , we have brought together all the known to us experimental data

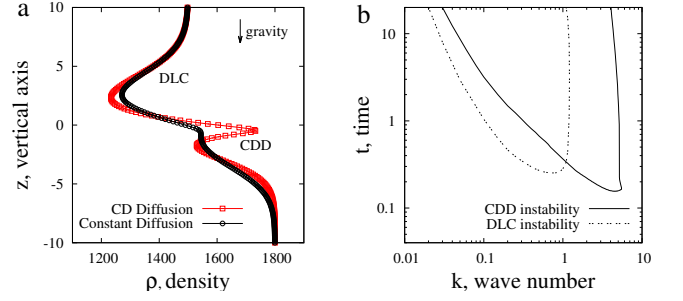


FIG. 2: (a) Instantaneous base state profiles of the total density (9) for the case of constant diffusion (circles) and concentration-dependent diffusion (squares) at  $t = 5$ ; (b) Neutral curves for DLC and CDD instabilities which arise in two zones low in density shown in Fig. 2a.

(see Supplementary information A) and have obtained

$$\begin{aligned} D_a(A) &\approx 0.158A + 0.881, \\ D_b(B) &\approx -0.087B + 0.594, \\ D_s(S) &\approx -0.284S + 0.478. \end{aligned} \quad (8)$$

It follows from (8) that the salt is most immobile, compared with acid and base. In addition, the diffusivity of salt decreases with the growth of the salt concentration. All these factors together produce an interesting effect. In order to describe it in term of the buoyancy it is convenient to introduce the total dimensionless density:

$$\rho(x, z) = R_a A(x, z) + R_b B(x, z) + R_s S(x, z). \quad (9)$$

The base state profiles for the density (9) are shown in Fig. 2a for two different diffusion laws: (i) the constant diffusion with standard table values for coefficients; (ii) the concentration-dependent diffusion defined by (8). We see that the curve has only one minimum above the reaction front in the case (i) versus two minima (above and below the reaction front) in the case (ii). The lower minimum enclosed within the regions with a stable stratification occurs because of the progressively slower diffusion of the salt resulting in its accumulation in or near the reaction front. Both minima enable for the potential development of the instability in the presence of gravity. The upper minimum is the typical for the DLC instability (Fig. 2a, squares). The lower local minimum on the same curve is much more interesting: since it has appeared exclusively due to the concentration-dependence of diffusion, we have named it as the CDD instability.

A nonsteady spectral amplitude problem has been solved by the method suggested originally in [23] and developed for chemo-convection in [8, 9]. Fig. 2b shows the neutral curves for the DLC and CDD instabilities. At time  $t \approx 0.15$  the CDD disturbance with a wave number  $k \approx 4.6$  is the first to lose stability. Then more and more waves are involved into the instability area. The DLC instability arises at  $t \approx 0.25$ , and its critical wave

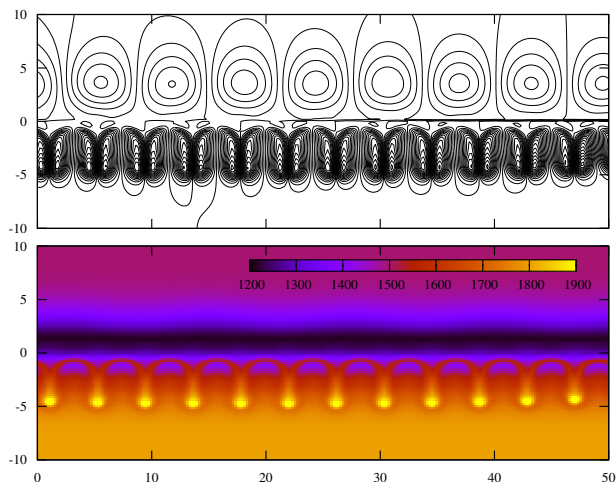


FIG. 3: Stream function (top) and total density (bottom) obtained by numerically solving full non-linear set of equations (1-8) for time  $t = 3$ . The line  $z = 0$  corresponds to the initial contact line between layers. Non-linear development of the CDD instability below the contact line is clearly seen.

number at the very beginning is  $k \approx 0.75$ . Eventually the maximum growth rate of disturbances in the instability balloon is shifted towards longer wavelengths.

To see non-linear development of the disturbances, the problem (1-8) has been solved numerically by a finite-difference method described [8] in detail. Stream lines and total density of the pattern at time  $t = 3$  are presented in Fig. 3. We found that in both zones low in density the convection develops independently (Fig. 3, top). The most interesting situation is in the lower area where the cellular chemoconvection with a perfectly periodic structure induced by the CDD instability has been observed. As in the experiment, the boundaries of the structure slowly move apart with time (Fig. 1e). At  $t = 3$  the pattern wavelength is about 4.2, which is in good agreement with the experimental data (Fig. 1d).

*Discussion and closing remarks.* – The system of miscible fluids when a given solution is placed above a denser solution with the fastest diffusing species in the upper layer has been classified in [10] as a typical case of the DLC instability. It occurs due to the formation of a depleted zone low in density which develops above the initial contact line while an accumulation zone where the density is maximal is obtained below the line. As a result, irregular DLC fingering is observed which develops on both sides of the initial contact line. In our case we also can identify the DLC plumes above initial reaction front (see the upper zone in Fig. 1a and Fig. 3). But below the contact line we meet a new kind of instability. It may occur only in the reactive case when an emerging component starts to accumulate near the reaction front. If its molecules quickly leave the reaction zone, then it has no significant influence on the instability scenario. But if the diffusion coefficient of the reaction product

decreases with growth of its concentration (the CDD effect), it can progressively make a local minimum in the density profile (figuratively, “density pocket”). Finally, under gravity condition one can observe the development of the localized cellular convection within the bulk of the motionless liquid (see the lower zone Fig. 1a and Fig. 3).

After the localized CDD structure occasionally was found in the pair  $\text{HNO}_3/\text{NaOH}$ , we have tested a number of other systems and found a similar patterning there. In our opinion, it may indicate that the discovered effect is of a general nature and should be taken into account in reaction-diffusion-convection problems as another tool to organize the movement of the reacting fluids. The CDD effect should take its place among other instabilities (DD, DDD, DLC) of the family of the double-diffusive phenomena introduced in physics over 60 years ago [20].

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